

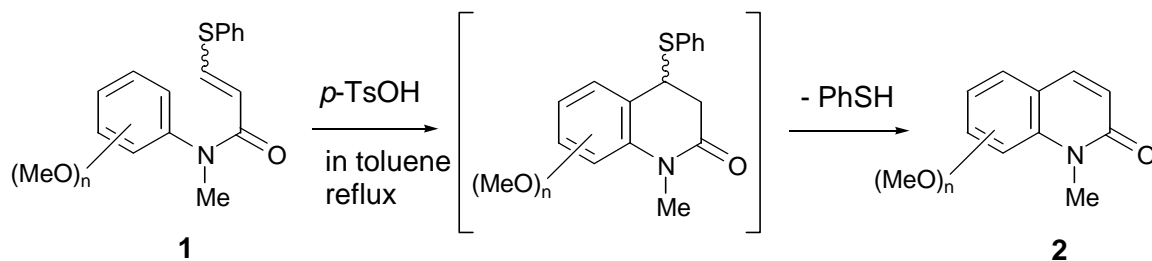
**SYNTHESIS OF 1,2-DIHYDROBENZ[c]AZEPIN-3-ONE VIA  
ACID-CATALYZED CYCLIZATION OF N-ARYLMETHYL-N-  
METHYL-3-PHENYLSULFANYLACRYLAMIDE**

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**Abstract** - Treatment of *N*-arylmethyl-*N*-methyl-*cis*-3-phenylsulfanyl acrylamide (**5**) with *p*-toluenesulfonic acid induced two reactions; cyclization to 1,2-dihydrobenz[*c*]azepin-3-ones (**7**) and *N*-dearylmethylation to *N*-methylacrylamides (**9** and **10**) depending on the structures of the substrates. The route provides a simple method of preparing 6-methoxy- (**7e**), 8-methoxy- (**7d**), 6,8-dimethoxy- (**7f**), and 8,9-dimethoxy-*N*-methyl-1,2-dihydrobenz[*c*]azepin-3-ones (**7g**), although the scope is limited by some side reactions.

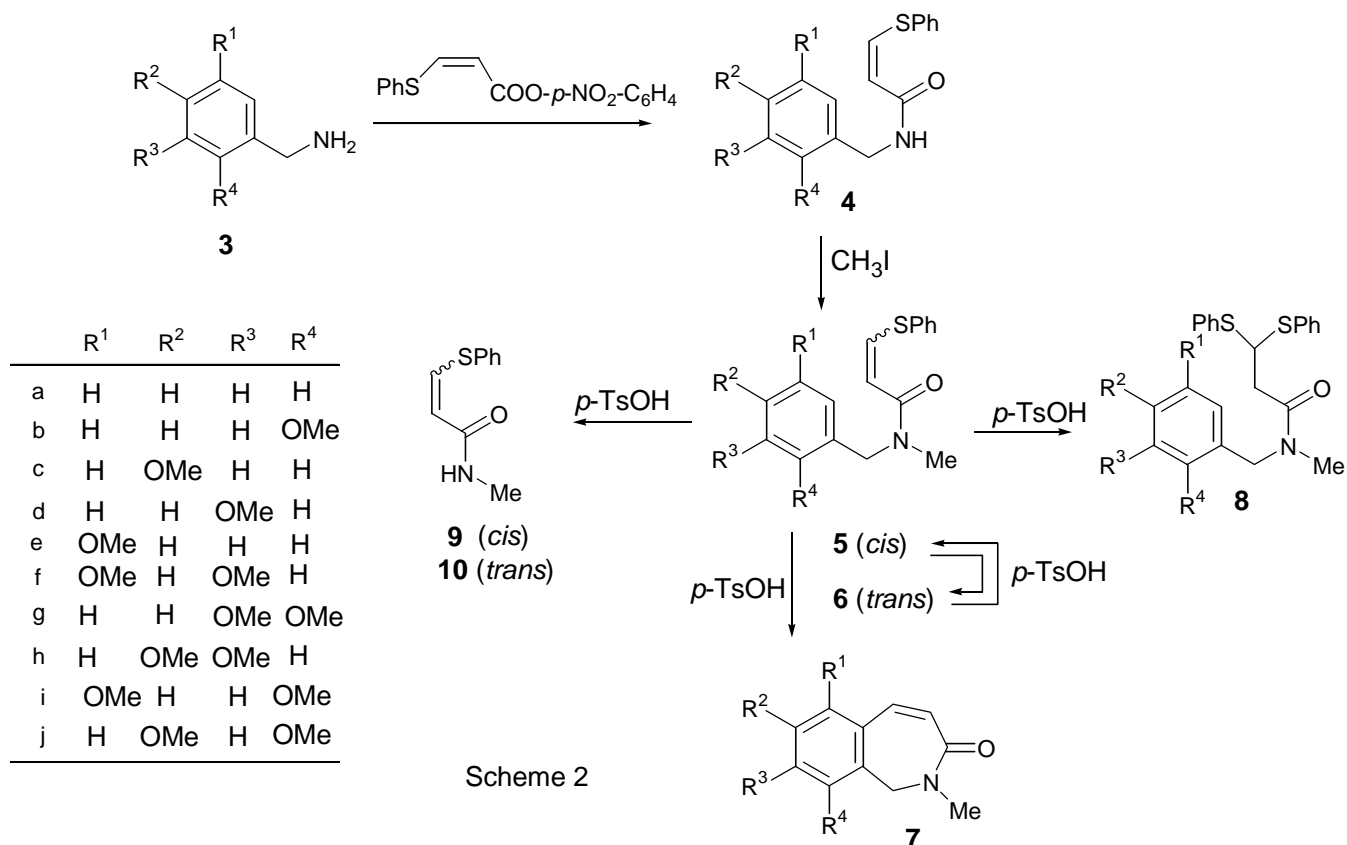
In a series of papers we reported the syntheses of 1,2,3,4-tetrahydroisoquinolines,<sup>1</sup> 1,2,3,4-tetrahydroquinolines,<sup>2</sup> 2,3,4,5-tetrahydro-1*H*-3-benzazepines,<sup>3</sup> and 2,3,4,5-tetrahydro-1*H*-2-benzazepines,<sup>4</sup> using an aromatic cyclization of the sulfonium ion formed *in situ* from a sulfinyl precursor (Pummerer reaction). During the course of the investigations we found that *N*-aryl-*N*-methyl-3-phenylsulfanylacrylamides (**1**) on treatment with *p*-toluenesulfonic acid (*p*-TsOH) in toluene under reflux induced the cyclization to produce 2-quinolones (**2**), providing a convenient



Scheme 1

method for the construction of 2-quinolone ring system.<sup>5</sup> In this paper we describe an acid-catalyzed cyclization of *N*-arylmethyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (**5**), which may provide a method of preparing 1,2-dihydrobenz[*c*]azepin-3-ones.<sup>6</sup>

The preparation of **5** was readily achieved by acylation of arylmethanamines (**3**) with *p*-nitrophenyl *cis*-3-(phenylsulfanyl)acrylate, followed by methylation of the resulting acrylamide (**4**) with methyl iodide in the presence of a phase transfer catalyst.



Scheme 2

The treatment of **5** with *p*-TsOH in toluene or benzene under reflux for appropriate times yielded various products, depending on the structure of *N*-arylmethyl moiety. The products included the *trans* geometric isomer (**6**), 1,2-dihydrobenz[*c*]azepin-3-one (**7**), a thioacetal (**8**), *N*-methyl-*cis*-acrylamide (**9**) and *N*-methyl-*trans*-acrylamide (**10**). The products were well characterized by MS, IR, and <sup>1</sup>H- and

<sup>13</sup>C-NMR spectral data. The results were collected in Table 1.

Table 1 Reactions of *N*-Arylmethyl-3-phenylsulfanylacrylamides (**5**) and (**6**) with *p*-TsOH under reflux

Run	Substrates	Solvent	Time (h)	Yields (Products)					
				<i>N</i> -Arylmethyl-acrylamide		Azepinone	Thioacetal	Acrylamides	
				<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
1	<b>5a</b>	toluene	0.5	--	61 ( <b>6a</b> )	--	13 ( <b>8a</b> )	--	--
2	<b>5b</b>	toluene	0.8	--	44 ( <b>6b</b> )	--	--	--	42
3	<b>5c</b>	toluene	0.25	--	--	--	--	--	41
4	<b>5d=5e</b>	toluene	0.75	--	--	77 ( <b>7d</b> )	--	--	--
				--	--	15 ( <b>7e</b> )	--	--	--
5	<b>5f</b>	toluene	5	7 ( <b>5f</b> )	8 ( <b>6f</b> )	74 ( <b>7f</b> )	--	--	--
6	<b>6f</b>	toluene	3	--	--	73 ( <b>7f</b> )	--	--	--
7	<b>5g</b>	toluene	5	4 ( <b>5g</b> )	11 ( <b>6g</b> )	48 ( <b>7g</b> )	7 ( <b>8g</b> )	--	--
8	<b>6g</b>	toluene	5	3 ( <b>5g</b> )	11 ( <b>6g</b> )	55 ( <b>7g</b> )	5 ( <b>8g</b> )	--	--
9	<b>5h</b>	benzene	4	--	--	1 ( <b>7h</b> )	--	6	45
10	<b>6h</b>	benzene	4	--	--	--	--	3	57
11	<b>5i</b>	benzene	4	5 ( <b>5i</b> )	38 ( <b>6i</b> )	--	3 ( <b>8i</b> )	--	26
12	<b>5j</b>	toluene	1	--	--	--	--	--	45

The substrates (**5d**, **5f**, and **5g**) which have an OMe group *para* to the reaction center of the phenyl ring, caused the cyclization to give the benz[*c*]azepin-3-ones (**7**) in good to moderate yields (Runs 4, 5 and 7).

The reaction of the *trans*-isomer (**6f** and **6g**) with *p*-TsOH also induced the cyclization to produce the respective benz[*c*]azepin-3-ones (**7f** and **7g**) in moderate yields (Runs 6 and 8).

However, the cyclization of **5h**, in spite of bearing a *para*-OMe group which should activate the reactive center, hardly occurred to yield **7h** in trace amount (Yield: 1%) (Run 9). Instead, this reaction mainly caused the elimination of *N*-arylmethyl group to give **9** (6%) and **10** (45%). This result demonstrated that the *N*-dearylmethylation reaction occurred in preference to the ring-closure reaction, suggesting that the OMe ( $R^2$  in **5h**) *para* to the *N*-arylmethyl group facilitated the *N*-dearylmethylation reaction. In

accordance to this observation the other substrates (**5b**, **5c**, **5i**, and **5j**) having an OMe *para* or *ortho* to the *N*-arylmethyl group mainly yielded the *N*-dearylmethylation products (**9** and **10**) (Runs 2, 3, 11, and 12).

The reaction of the substrate (**5a**) bearing no OMe group caused only the geometrical isomerization of the double bond to yield the *trans*-isomer (**6a**) in 61 % yield (Run 1). Neither cyclization nor *N*-debenzylation occurred to any extent.

The results described above clearly revealed that the OMe group, if the group is present at the positions which can activate each reaction centers, enhanced not only the cyclization reaction but also the *N*-dearylmethylation reaction. Thus, this route provides a convenient method for preparing 6-methoxy- (**7e**), 8-methoxy- (**7d**), 6,8-dimethoxy- (**7f**), and 8,9-dimethoxy-*N*-methyl-1,2-dihydrobenz[*c*]azepin-3-ones (**7g**), although the scope is fairly limited by the inevitable side reactions.

## ACKNOWLEDGMENT

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## EXPERIMENTAL

**General Notes** Unless otherwise noted, the following procedures were adopted. Melting points were taken on a Yanagimoto SP-M1 hot-stage melting point apparatus and are uncorrected. IR spectra were obtained as films for oils and gums, and KBr disks for solids with a JASCO FT/IR-5000 spectrophotometer, and are given in  $\text{cm}^{-1}$ . NMR spectra were measured on a JEOL JNM-AL 300 ( $^1\text{H-NMR}$ , 300 MHz;  $^{13}\text{C-NMR}$ , 75 MHz) NMR spectrometer in  $\text{CDCl}_3$  with tetramethylsilane as an internal standard at room temperature and the chemical shifts are given in  $\delta$  values. UV spectra were measured with a Hitachi U-3200 spectrophotometer in dioxane and values are given in  $\lambda_{\text{max}}$  nm ( $\epsilon$ ). LR-MS were taken on JMS-AM20, and high resolution MS (HR-MS) on a JEOL JMS-D300 spectrometer at 70 eV (EI-MS) or at 270 eV [(CI-MS), reactant gas: *iso*-butane] using direct or GC/MS inlet systems. FAB-MS spectra were recorded with JEOL-HX100A spectrometer using glycerol as a matrix. Elemental analyses were recorded on a Yanaco-CHN-corder MT-3. TLC was performed on Merck precoated Silica

gel 60 F<sub>254</sub> plates (Merck). Column chromatography was carried out with silica gel (Wakogel C-200). The organic extract from each reaction mixture was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated *in vacuo* to dryness.

### Preparation of *N*-arylmethyl-*cis*-(3-phenylsulfanyl)acrylamide (**4**)

#### i) Preparation of *p*-nitrophenyl 3-phenylsulfanylacrylate

To a solution of *cis*-3-phenylsulfanylacrylic acid (1.0 g, 5.6 mmol), and *p*-nitrophenol (0.93 g, 7.0 mmol) in CHCl<sub>3</sub> (50 mL) dicyclohexylcarbodiimide (DCC) (1.14 g, 5.5 mmol) was added at 0 °C, and the mixture was stirred at rt for 1 h. After removal of crystalline precipitates by filtration, the filtrate was condensed *in vacuo*. The residue was recrystallized from CHCl<sub>3</sub> to give the ester (1.12 g, 67%) as colorless needles, mp 153-156 °C. IR: 3325, 1707. <sup>1</sup>H-NMR: 6.13 (1H, d, *J*=10 Hz, olefinic H), 7.3-7.5 (7H, m, PhH), 7.58 (1H, d, *J*=10 Hz, olefinic H), 8.29 (2H, d, *J*=9 Hz, PhH). EI-LRMS *m/z*: 301 (M<sup>+</sup>, 20), 163 (M<sup>+</sup>-138, base peak). *Anal.* Calcd for C<sub>15</sub>H<sub>11</sub>NO<sub>4</sub>S: C, 59.79; H, 3.68; N, 4.65. Found: C, 59.79; H, 3.96; N, 4.62.

#### ii) Acylation of aryethylamine (**3**) with *p*-nitrophenyl 3-phenylsulfanylacrylate (General procedure)

A solution of *p*-nitrophenyl 3-phenylsulfanylacrylate (1.1 mol eq.), **3** (1 mol eq.), and Et<sub>3</sub>N (1.2 mol eq.) in CHCl<sub>3</sub> (100 mL) was stirred at rt for 48 h. After evaporation of the solvent *in vacuo*, the residue was chromatographed over SiO<sub>2</sub> eluted with AcOEt to give **4**.

*N*-Benzyl-*cis*-3-phenylsulfanylacrylamide (**4a**) (5.45 g, 78%) was obtained from **3a** (2.8 g, 26 mmol) as colorless needles recrystallized from acetone-Et<sub>2</sub>O, mp 155-157 °C. IR: 3288, 1631. <sup>1</sup>H-NMR: 4.51 (1H, d, *J*=6 Hz, CH<sub>2</sub>NH), 4.58 (1H, d, *J*=6 Hz, CH<sub>2</sub>NH), 5.83 (1H, d, *J*=10 Hz, olefinic H), 7.11 (1H, d, *J*=10 Hz, olefinic H), 7.3-7.5 (10H, m, PhH and SPhH). EI-LRMS *m/z*: 269 (M<sup>+</sup>), 160 (M<sup>+</sup>-109, base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>16</sub>H<sub>15</sub>NOS: 269.0874, Found: 269.0870.

*N*-(2-Methoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (**4b**) (3.26 g, 65%) was obtained from **3b** (2.05 g, 15 mmol) as colorless needles recrystallized from acetone-Et<sub>2</sub>O, mp 123-125 °C. IR: 3269,

1624. <sup>1</sup>H-NMR: 3.85 (3H, s, OCH<sub>3</sub>), 4.53 (2H, d, *J* = 6 Hz, CH<sub>2</sub>NH), 5.81 (1H, d, *J* = 10 Hz, olefinic H), 7.03 (1H, d, *J* = 10 Hz, olefinic H), 6.8-7.5 (9H, m, ArH and SPhH). <sup>13</sup>C-NMR: 38.9 (C1'), 55.1 (OCH<sub>3</sub>), 110.1 (ArCH), 115.7 (ArCH), 120.5 (C2), 126.3 (PhC), 127.5 (ArCH), 128.6 (ArCH), 129.0 (PhCHx<sub>2</sub>), 129.6 (PhCH), 130.6 (PhCHx<sub>2</sub>), 137.3 (ArC), 144.4 (C3), 157.3 (ArC), 165.7 (C1). EI-LRMS *m/z*: 299 (M<sup>+</sup>), 190 (M<sup>+</sup>-109). *Anal.* Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>S: C, 68.20; H, 5.72; N, 4.68. Found: C, 67.99; H, 5.78; N, 4.62.

***N*-(4-Methoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4c)** (3.65 g, 73%) was obtained from **3c** (2.05 g, 15 mmol) as colorless needles recrystallized from CHCl<sub>3</sub>-Et<sub>2</sub>O, mp 155-156 °C. IR: 3293, 1629. <sup>1</sup>H-NMR: 3.79 (3H, s, OCH<sub>3</sub>), 4.46 (2H, d, *J* = 6 Hz, CH<sub>2</sub>NH), 5.82 (1H, d, *J* = 10 Hz, olefinic H), 7.08 (1H, d, *J* = 10 Hz, olefinic H), 6.8-7.6 (9H, m, ArH and SPhH). <sup>13</sup>C-NMR: 43.2 (C1'), 55.3 (OCH<sub>3</sub>), 114.1 (ArCHx<sub>2</sub>), 118.0 (C2), 128.8 (PhCH), 129.3 (PhCHx<sub>2</sub>), 129.5 (PhCHx<sub>2</sub>), 130.2 (PhC), 131.2 (ArC), 132.7 (ArCHx<sub>2</sub>), 142.8 (C3), 159.0 (ArC), 164.1 (C2). EI-LRMS *m/z*: 299 (M<sup>+</sup>), 190 (M<sup>+</sup>-109, base peak). *Anal.* Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>S: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.04; H, 6.02; N, 4.82).

***N*-(3-Methoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4d)** (3.21 g, 65%) was obtained from **3d** (2.05 g, 15 mmol) as colorless plates recrystallized from CHCl<sub>3</sub>-Et<sub>2</sub>O, mp 113-115 °C. IR: 3307, 1630. <sup>1</sup>H-NMR: 3.80 (3H, s, OCH<sub>3</sub>), 4.51 (2H, d, *J* = 6 Hz, CH<sub>2</sub>NH), 5.84 (1H, d, *J* = 10 Hz, olefinic H), 7.09 (1H, d, *J* = 10 Hz, olefinic H), 6.8-7.5 (9H, m, ArH and SPhH). EI-LRMS *m/z*: 299 (M<sup>+</sup>), 190 (M<sup>+</sup>-109, base peak). *Anal.* Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>2</sub>S: C, 68.20; H, 5.72; N, 4.68. Found: C, 68.04; H, 6.02; N, 4.82.

***N*-(3,5-Dimethoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4f)** (3.45 g, 70 %) was obtained from **3f** (2.505 g, 15 mmol) as colorless needles recrystallized from CHCl<sub>3</sub>-Et<sub>2</sub>O, mp 119-121 °C. IR: 3302, 1633, 1597. <sup>1</sup>H-NMR: 3.77 (6H, s, OCH<sub>3</sub>), 4.47 (2H, d, *J* = 6 Hz, -CH<sub>2</sub>NH-), 5.84 (1H, d, *J* = 10 Hz, olefinic H), 6.3-6.5 (3H, m, ArH), 7.09 (1H, d, *J* = 10 Hz, olefinic H), 7.3-7.6 (5H, m, SPhH). <sup>13</sup>C-NMR: 43.4 (C1'), 55.3 (OCH<sub>3</sub>x<sub>2</sub>), 99.4 (ArCH), 105.7 (ArCHx<sub>2</sub>), 115.3 (C2), 127.7 (PhCH), 129.1 (PhCHx<sub>2</sub>), 130.8 (PhCHx<sub>2</sub>), 137.2 (PhC), 140.7 (ArC), 145.3 (C3), 161.0 (ArCx<sub>2</sub>), 165.9 (C2). FAB-LRMS *m/z*:

330 (MH<sup>+</sup>, base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>S: 330.1164, Found: 330.1146.

***N*-(2,3-Dimethoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4g)** (3.21 g, 65 %) was obtained from **3f** (2.505 g, 15 mmol) as colorless needles recrystallized from CHCl<sub>3</sub>-Et<sub>2</sub>O, mp 145-147 °C. IR: 3305, 1627, 1597. <sup>1</sup>H-NMR: 3.86 (3H, s, OCH<sub>3</sub>), 3.88 (3H, s, OCH<sub>3</sub>), 4.54 (2H, d, *J*=6 Hz, CH<sub>2</sub>NH), 5.80 (2H, d, *J*=10 Hz, olefinic H), 6.8-7.1 (4H, m, olefinic H and ArH), 7.2-7.6 (5H, m, SPhH). FAB-LRMS *m/z*: 330 (MH<sup>+</sup>, base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>18</sub>H<sub>20</sub>NO<sub>3</sub>S: 330.1164, Found: 330.1158.

***N*-(3,4-Dimethoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4h)** (299 mg, 54%) was obtained from **3h** (224 mg, 1.66 mmol) as colorless plates recrystallized from acetone-Et<sub>2</sub>O, mp 152-154 °C. IR: 3309, 1635. <sup>1</sup>H-NMR: 3.87 (3H, s, OCH<sub>3</sub>), 3.88 (3H, s, OCH<sub>3</sub>), 4.48 (2H, d, *J*=6 Hz, CH<sub>2</sub>NH), 5.76 (1H, s, NH), 5.83 (1H, d, *J*=10 Hz, olefinic H), 7.10 (1H, d, *J*=10 Hz, olefinic H), 6.8-7.5 (8H, m, ArH and SPhH). <sup>13</sup>C-NMR: 43.1 (C1'), 55.6 (OCH<sub>3</sub>), 55.7 (OCH<sub>3</sub>), 111.0 (ArCH), 111.1 (ArCH), 115.4 (C2), 120.1 (ArCH), 127.7 (PhCH), 129.1 (PhCHx2), 130.6 (PhCHx2), 130.8 (PhC), 137.0 (ArC), 145.0 (C2), 148.1 (ArC), 148.8 (ArC), 165.9 (C1). EI-LRMS *m/z*: 329 (M<sup>+</sup>), 220 (base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S: 329.1086, Found: 329.1107.

***N*-(2,4-Methoxyphenyl)methyl-*cis*-3-phenylsulfanylacrylamide (4j)** (3.36 g, 68 %) was obtained from **3f** (2.505 g, 15 mmol) as colorless needles recrystallized from CHCl<sub>3</sub>-Et<sub>2</sub>O, mp 140-142 °C. IR: 3259, 1626, 1508. <sup>1</sup>H-NMR: 3.79 (3H, s, OCH<sub>3</sub>), 3.82 (3H, s, OCH<sub>3</sub>), 4.46 (2H, d, *J*=6 Hz, CH<sub>2</sub>NH), 5.79 (1H, d, *J*=10 Hz, olefinic H), 6.4-6.5 (3H, m, ArH), 7.02 (1H, d, *J*=10 Hz, olefinic H), 7.2-7.6 (5H, m, SPhH). EI-LRMS *m/z*: 329 (M<sup>+</sup>), 220 (base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>3</sub>S: 329.1086, Found: 329.1100.

#### **Preparation of *N*-arylmethyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamides (5) (General Procedure)**

A solution of **4** (1.0 mol eq.), 85% KOH (10 mol eq.), CH<sub>3</sub>I (10 mol eq.), and tetraethylammonium bromide (TEAB) (0.5 mol eq.) in THF (100 mL) was allowed to stand at rt for 16 h under stirring. The reaction mixture was extracted with CHCl<sub>3</sub>. The product was purified by column chromatography over

SiO<sub>2</sub> eluted with ethyl acetate/hexane (1:1) to give **5**.

**N-Benzyl-N-methyl-cis-3-phenylsulfanylacrylamide (5a)** (2.58g, 62%) was obtained from **4a** (4.0 g 15 mmol) as colorless prisms recrystallized from acetone-Et<sub>2</sub>O, mp 63-64 °C. IR: 1625. <sup>1</sup>H-NMR: 2.97, 3.04 (total 3H, each s, NCH<sub>3</sub>), 4.59, 4.68 (total 2H, each br s, CH<sub>2</sub>NCH<sub>3</sub>), 6.25, 6.29 (total 1H, each d, *J*=10 Hz, olefinic H), 7.1-7.5 (11H, m, olefinic H, PhH and SPhH). EI-LRMS *m/z*: 283 (M<sup>+</sup>), 174 (M<sup>+</sup>-109, base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>17</sub>H<sub>17</sub>NO<sub>3</sub>S: 283.1029, Found: 283.1031.

**N-(2-Methoxyphenyl)methyl-N-methyl-cis-3-phenylsulfanylacrylamide (5b)** (880 mg, 84%) was obtained from **4b** (1.0 g, 3 mmol) as colorless prates recrystallized from acetone-Et<sub>2</sub>O, mp 80-82 °C. IR: 1624. <sup>1</sup>H-NMR: 3.02, 3.05 (total 3H, each s, NCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 4.57, 4.73 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 6.23, 6.30 (total 1H, each d, *J*=10 Hz, olefinic H), 7.09 (1H, *J*=10 Hz, olefinic H), 6.8-7.2 (9H, m, ArH and SPhH). <sup>13</sup>C-NMR: 33.8 (NCH<sub>3</sub>), 48.8 (C1'), 55.0 (OCH<sub>3</sub>), 110.0 (ArCH), 112.5 (C2), 120.5 (ArCH), 124.6 (PhC), 126.9 (ArCH), 127.5 (PhCH), 128.4 (ArCH), 129.0 (PhCHx2), 130.6 (PhCHx2), 137.7 (ArC), 146.5 (C3), 156.8 (ArC), 167.2 (C1). EI-LRMS *m/z*: 313 (M<sup>+</sup>), 204 (M<sup>+</sup>-109, base peak). *Anal.* Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 68.98; H, 6.11; N, 4.47. Found: C, 68.82; H, 6.15; N, 4.35.

**N-(4-Methoxyphenyl)methyl-N-methyl-cis-3-phenylsulfanylacrylamide (5c)** (840 mg, 81%) was obtained from **4c** (1.0 g, 3 mmol) as colorless prates recrystallized from ethyl acetate-Et<sub>2</sub>O, mp 60-62 °C. IR: 3293, 1629. <sup>1</sup>H-NMR: 3.03, 3.06 (total 3H, each s, NCH<sub>3</sub>), 3.79 (3H, s, OCH<sub>3</sub>), 4.58, 4.74 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 6.24, 6.32 (total 1H, each d, *J*=10 Hz, olefinic H), 7.08 (1H, d, *J*=10 Hz, olefinic H), 6.8-7.6 (9H, m, ArH and SPhH). EI-LRMS *m/z*: 299 (M<sup>+</sup>), 190 (M<sup>+</sup>-109, base peak). *Anal.* Calcd for C<sub>18</sub>H<sub>19</sub>NO<sub>2</sub>S: C, 68.98; H, 6.11; N, 4.47. Found: C, 68.80; H, 6.20; N, 4.25.

**N-(3-Methoxyphenyl)methyl-N-methyl-cis-3-phenylsulfanylacrylamide (5d)** (0.77 g, 74%) was obtained from **4c** (1.0 g, 3 mmol) as a pale yellow gum. IR: 1628. <sup>1</sup>H-NMR: 2.98, 3.05 (total 3H, each s, NCH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 4.56, 4.66 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 6.24, 6.30 (total 1H, each d, *J*=10 Hz, olefinic H), 6.7-7.5 (10H, m, olefinic H, ArH and SPhH). LRMS *m/z*: 313 (M<sup>+</sup>), 204 (M<sup>+</sup>-109, base



peak). EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{18}H_{19}NO_3S$ : 313.1136, Found: 313.1120.

***N*-(3,5-Dimethoxyphenyl)methyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (5f)** (960 mg, 92%) was obtained from **4f** (1 g, 3.05 mmol) as a yellow gum. IR: 1627.  $^1H$ -NMR: 2.98, 3.06 (total 3H, each br s,  $NCH_3$ ), 3.78 (6H, s,  $OCH_3$ ), 4.52, 4.63 (total 2H, each br s,  $CH_2NCH_3$ ), 6.2-6.5 (4H, m, olefinic H and ArH), 7.2-7.6 (6H, m, olefinic H and SPhH).  $^{13}C$ -NMR: 33.8, 34.6 ( $NCH_3$ ), 50.5, 53.4 ( $C1'$ ), 55.2 ( $OCH_3 \times 2$ ), 99.1 (ArCH), 104.2 (ArCH), 105.9 (ArCH), 112.0 (C2), 127.6 (PhCH), 129.0 (PhCH $\times 2$ ), 130.6 (PhCH $\times 2$ ), 137.5 (PhC), 139.2, 139.6 (ArC), 147.0 (C3), 160.9, 161.2 (ArC), 166.4, 167.0 (C1). EI-LRMS  $m/z$ : 343 ( $M^+$ ), 234 (base peak). FAB-HRMS ( $MH^+$ )  $m/z$  Calcd for  $C_{19}H_{22}NO_3S$ : 344.1321, Found: 344.1302.

***N*-(2,3-Dimethoxyphenyl)methyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (5g)** (4.3 g, 98%) was obtained from **4g** (4.2 g, 12.8 mmol) as a colorless gum. IR: 1628, 1477.  $^1H$ -NMR: 2.99, 3.05 (total 3H, each br s,  $NCH_3$ ), 3.84 (3H, s,  $OCH_3$ ), 3.87 (3H, s,  $OCH_3$ ), 4.61, 4.77 (total 2H, each br s,  $CH_2NCH_3$ ), 6.28 (1H, br d,  $J=10$  Hz, olefinic H), 6.7-7.5 (9H, m, olefinic H, ArH and SPhH). EI-LRMS  $m/z$ : 343 ( $M^+$ ), 234 (base peak). FAB-HRMS ( $MH^+$ )  $m/z$  Calcd for  $C_{19}H_{22}NO_3S$ : 344.1321, Found: 344.1333.

***N*-(3,4-Dimethoxyphenyl)methyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (5h)** (5.02 g, 99%) was obtained from **4h** (4.87 g, 14.5 mmol) as a pale yellow gum. IR: 1623.  $^1H$ -NMR: 2.96, 3.05 (total 3H, each s,  $NCH_3$ ), 3.86 (3H, s,  $OCH_3$ ), 3.88 (3H, s,  $OCH_3$ ), 4.54, 4.63 (total 2H, each s,  $CH_2NCH_3$ ), 6.28, 6.30 (1H, d,  $J=10$  Hz, olefinic H), 6.7-6.9 (3H, m, ArH), 7.17, 7.22 (1H, d,  $J=10$  Hz, olefinic H), 7.3-7.5 (5H, m, SPhH).  $^{13}C$ -NMR: 34.2, 33.4 ( $NCH_3$ ), 50.0, 52.9 ( $C1'$ ), 55.6 ( $OCH_3 \times 2$ ), 109.2, 110.7 (ArCH), 111.1, 111.2 (ArCH), 111.9, 112.1 (C2), 118.3, 120.4 (ArCH), 127.5 (PhCH), 128.9 (PhCH $\times 2$ ), 129.6, 137.3 (PhC), 130.4 (PhCH $\times 2$ ), 146.7, 146.9 (C3), 148.1 (ArC), 148.8 (ArC), 149.0 (ArC), 166.2, 166.8 (C1). EI-LRMS  $m/z$ : 343 ( $M^+$ ), 234 (base peak). EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{19}H_{21}NO_3S$ : 343.1240, Found: 343.1215.

***N*-(2,5-Dimethoxyphenyl)methyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (5i)**

A solution of *p*-nitrophenyl 3-phenylsulfanylacrylate (1.48 g, 4.9 mmol), *N*-(2,5-dimethoxyphenyl)-methyl-*N*-methylamine (887 mg, 4.9 mmol) and Et<sub>3</sub>N (0.8 mL, 4.9 mmol) in CHCl<sub>3</sub> (50 mL) was stirred at rt for 40 h and refluxed for 4 h. The reaction mixture was extracted with CHCl<sub>3</sub>. After removal of the solvent *in vacuo*, the residue was chromatographed over SiO<sub>2</sub> eluted with AcOEt/hexane (1:2) to give **5i** (1.30g, 78%) as a pale yellow oil. IR: 1629 cm<sup>-1</sup>. <sup>1</sup>H-NMR: 3.02, 3.06 (total 3H, each s, NCH<sub>3</sub>), 3.75 (3H, s, OCH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 4.54, 4.71 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 6.22 (1H, d, *J*=10 Hz, olefinic H), 6.7-6.9 (3H, m, ArH), 7.10 (1H, d, *J*=10 Hz, olefinic H), 7.29-7.52 (5H, m, SPhH). <sup>13</sup>C-NMR: 34.0, 35.5 (NCH<sub>3</sub>), 45.2, 48.9 (C1'), 55.7 (OCH<sub>3</sub>), 55.6, 55.7, 55.9 (OCH<sub>3</sub>), 111.0, 111.3 (ArCH), 112.3, 112.5 (ArCH), 113.7 (C2), 115.3 (ArCH), 126.0, 126.6 (PhC), 127.7 (PhCH), 129.6 (PhCH<sub>2</sub>), 130.8 (PhCH<sub>2</sub>), 137.7 (ArC), 146.7, 146.9 (C3), 151.0, 151.8 (ArC), 153.7, 153.8 (ArC), 167.4, 166.7 (C1). EI-LRMS *m/z*: 343 (M<sup>+</sup>), 234 (base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S: 344.1321, Found: 344.1310.

***N*-(2,4-Dimethoxyphenyl)methyl-*N*-methyl-*cis*-3-phenylsulfanylacrylamide (5j)** (933 mg, 97%) was obtained from **4j** (920 mg, 2.8 mmol) as a yellow gum. IR: 1624, 1508. <sup>1</sup>H-NMR: 3.02 (3H, br s, NCH<sub>3</sub>), 3.80 (3H, s, OCH<sub>3</sub>), 3.83 (3H, s, OCH<sub>3</sub>), 4.49, 4.65 (total 2H, each br s, CH<sub>2</sub>NCH<sub>3</sub>), 6.28 (1H, d, *J*=10 Hz, olefinic H), 6.4-6.6 (3H, m, ArH), 6.9-7.6 (6H, m, olefinic H). EI-LRMS *m/z*: 343 (M<sup>+</sup>), 234 (base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>19</sub>H<sub>21</sub>NO<sub>3</sub>S: 343.1240, Found: 343.1215.

**Acid-catalyzed Reaction of 5 with *p*-TsOH- General Procedure:** A solution of **5** (1 mol eq.) and *p*-TsOH (1.5 mol eq.) in toluene or benzene (50 mL) was heated under reflux for appropriate times shown in Table 1. The reaction mixture was extracted with CHCl<sub>3</sub>. The products were purified by column chromatography (AcOEt / hexane 1:1), MPTLC (AcOEt / hexane 2:3), and PTLC (AcOEt / hexane 2:3).

Run 1: **5a** (500 mg, 1.77 mmol) yielded **6a** (303 mg, 61%) and **8a** (48 mg, 13%).

***N*-Benzyl-*N*-methyl-*trans*-3-phenylsulfanylacrylamide (6a)** A Pale yellow gum. IR: 1639. <sup>1</sup>H-NMR: 2.95 (3H, br s, NCH<sub>3</sub>), 4.59 (2H, br s, CH<sub>2</sub>NCH<sub>3</sub>), 6.24 (1H, d, *J*=15 Hz, olefinic H), 7.3-7.4 (10H, m, PhH, SPhH), 7.83 (1H, d, *J*=15 Hz, olefinic H). LRMS *m/z*: 283 (M<sup>+</sup>), 91 (M<sup>+</sup>-192, base peak).

EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{17}H_{17}NO_3S$ : 283.1029, Found: 283.1000.

***N*-Benzyl-*N*-methyl-3,3-diphenylsulfanylpropylamide (8a)** A Pale yellow gum. IR: 1644.  $^1H$ -NMR: 2.81, 2.96 (total 3H, each s,  $NCH_3$ ), 2.88 (2H, d,  $J=7$  Hz,  $COCH_2$ ), 4.43, 4.60 (total 2H, each s,  $CH_2NCH_3$ ), 5.13, 5.14 (total 1H, each t,  $J=7$  Hz,  $CH(SPh)_2$ ), 7.2-7.6 (15H, m, PhH and SPhH). LRMS  $m/z$ : 393 ( $M^+$ ), 91 ( $M^+-302$ , base peak).

Run 2: **5b** (500 mg, 1.67 mmol) yielded **6b** (222 mg, 44%) and **10** (51 mg, 42%).

***N*-(2-Methoxyphenyl)methyl-*N*-methyl-*trans*-3-phenylsulfanylacrylamide (6b)**. A Pale yellow gum. IR: 1633.  $^1H$ -NMR: 2.98 (3H, s,  $NCH_3$ ), 3.81 (3H, s,  $OCH_3$ ), 4.46 (2H, br s,  $CHNCH_3$ ), 6.26 (1H, d,  $J=15$  Hz, olefinic H), 6.8-7.3 (9H, m, ArH and SPhH), 7.78 (1H, d,  $J=15$  Hz, olefinic H). EI-LRMS  $m/z$ : 313 ( $M^+$ , 1), 204 ( $M^+-109$ , 100). EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{18}H_{19}NO_3S$ : 313.1136, Found: 313.1145.

***N*-Methyl-*trans*-3-phenylsulfanylacrylamide (10)** Colorless plates recrystallized from acetone-Et<sub>2</sub>O, mp 106-109 °C. IR: 3274, 1637.  $^1H$ -NMR: 2.85 (3H, d,  $J=5$  Hz,  $NCH_3$ ), 5.68 (1H, d,  $J=15$  Hz, olefinic H), 7.3-7.6 (5H, m, SPhH), 7.67 (1H, d,  $J=15$  Hz, olefinic H).  $^{13}C$ -NMR: 26.3 ( $NCH_3$ ), 118.3 (C2), 128.6 (PhCH), 129.5 (PhCH<sub>2</sub>), 131.5 (PhC), 132.5 (PhCH<sub>2</sub>), 142.0 (C3), 165.1 (C1). EI-LRMS  $m/z$ : 193 ( $M^+$ ), 163 ( $M^+-30$ , base peak). EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{10}H_{11}NOS$ : 193.0558, Found: 193.0520.

Run 3: **5c** (500 mg, 1.67 mmol) yielded **10** (125 mg, 41%).

Run 4: **5d** (100 mg, 0.32 mmol) yielded **7d** (50 mg, 77%) and **7e** (10 mg, 15%).

**8-Methoxy-2-methyl-1,2-dihydrobenz[*c*]azepin-3-one (7d)** Colorless plates recrystallized from acetone-Et<sub>2</sub>O, mp 102-104 °C. IR: 1633.  $^1H$ -NMR: 3.09 (3H, s,  $NCH_3$ ), 3.86 (3H, s,  $OCH_3$ ), 4.19 (2H, s, 1-H), 6.28 (1H, d,  $J=12$  Hz, 4-H), 6.81 (1H, d,  $J=2$  Hz, 9-H), 6.90 (1H, dd,  $J=8$  Hz, 2 Hz, 7-H), 7.00 (1H, d,  $J=12$  Hz, 5-H), 7.29 (1H, d,  $J=8$  Hz, 6-H).  $^{13}C$ -NMR: 35.0 ( $NCH_3$ ), 53.5 (C1), 55.4 ( $OCH_3$ ), 113.2 (C7), 113.3 (C9), 125.3 (C4), 128.3 (C5a), 130.9 (C5), 136.1 (C6), 137.8 (C9a), 160.4 (C8), 166.6 (C3). EI-LRMS  $m/z$ : 203 ( $M^+$ , base peak). EI-HRMS ( $M^+$ )  $m/z$  Calcd for  $C_{12}H_{13}NO_2$ : 203.0946, Found: 203.0986. UV: 281 (15800).

**6-Methoxy-2-methyl-1,2-dihydrobenz[c]azepin-3-one (7e):** A pale yellow gum. IR: 1635. <sup>1</sup>H-NMR: 3.08 (3H, s, NCH<sub>3</sub>), 3.87 (3H, s, OCH<sub>3</sub>), 4.18 (2H, s, 1-H), 6.38 (1H, d, *J*=12 Hz, 4-H), 6.89 (1H, d, *J*=8 Hz, 7-H), 6.90 (1H, d, *J*=8 Hz, 9-H), 7.34 (1H, t, *J*=8 Hz, 8-H), 7.39 (1H, d, *J*=12 Hz, 5-H). EI-LRMS *m/z*: 203 (M<sup>+</sup>, base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub>: 203.0946, Found: 203.0911. UV: 302 (6600), 264 (10500).

Run 5: **5f** (200 mg, 0.58 mmol) yielded **6f** (16 mg, 8%), **7f** (100 mg, 74%) and **8f** (29 mg, 11%). Recovered **5f** (14 mg, 7%).

***N*-(3,5-Dimethoxyphenyl)methyl-*N*-methyl-*trans*-3-phenylsulfanylacrylamide (6f)** A yellow gum. IR: 1631. <sup>1</sup>H-NMR: 2.92 (3H, br s, NCH<sub>3</sub>), 3.77 (6H, s, OCH<sub>3</sub>), 4.40, 4.54 (total 2H, each br s, CH<sub>2</sub>NCH<sub>3</sub>), 6.1-6.4 (4H, m, olefinic H and ArH), 7.3-7.6 (5H, m, SPhH), 7.82 (1H, d, *J*=15 Hz, olefinic H). <sup>13</sup>C-NMR: 34.5 (NCH<sub>3</sub>), 52.1 (C1'), 55.1 (OCH<sub>3</sub>x2), 99.1 (ArCH), 104.5 (ArCH), 105.7 (ArCH), 115.2 (C2), 128.4 (PhCH), 129.3 (PhCH), 129.5 (PhCH), 131.9 (PhCHx2), 139.5 (PhC and ArC), 143.8 (C3), 160.8 (ArC), 161.0 (ArC), 165.2 (C1). EI-LRMS *m/z*: 343 (M<sup>+</sup>), 234 (base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S: 344.1321, Found: 344.1300.

**6,8-Dimethoxy-2-methyl-1,2-dihydrobenz[c]azepin-3-one (7f)** Colorless plates recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, mp 113-116 °C IR: 1641, 1608. <sup>1</sup>H-NMR: 3.07 (3H, s, NCH<sub>3</sub>), 3.84 (3H, s, OCH<sub>3</sub>), 3.86 (3H, s, OCH<sub>3</sub>), 4.13 (2H, s, CH<sub>2</sub>NCH<sub>3</sub>), 6.25 (1H, d, *J*=12 Hz, olefinic H), 6.42 (1H, d, *J*=2 Hz, ArH), 6.45 (1H, d, *J*=2 Hz, ArH), 7.32 (1H, d, *J*=12 Hz, olefinic H). <sup>13</sup>C-NMR: 34.8 (NCH<sub>3</sub>), 53.6 (C1), 55.4 (OCH<sub>3</sub>), 55.7 (OCH<sub>3</sub>), 97.5 (C5), 104.0 (C4), 117.7 (C5a), 124.2 (C7), 131.1 (C9), 139.2 (C9a), 158.7 (C6), 161.6 (C8), 167.1 (C2). EI-LRMS *m/z*: 233 (M<sup>+</sup>), 204 (base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>13</sub>H<sub>16</sub>NO<sub>3</sub>: 234.1130, Found: 234.1141. UV: 278 (14600).

***N*-(3,5-Dimethoxyphenyl)methyl-*N*-methyl-3,3-diphenylsulphonylpropionamide (8f)** A Yellow gum. IR: 1668. <sup>1</sup>H-NMR: 2.84 (3H, s, NCH<sub>3</sub>), 2.95 (2H, d, *J*=7 Hz, COCH<sub>2</sub>), 3.72 (3H, s, OCH<sub>3</sub>), 3.76 (3H, s, OCH<sub>3</sub>), 4.38, 4.55 (total 2H, each br s, CH<sub>2</sub>NCH<sub>3</sub>), 5.12, 5.14 (total 1H, each t, *J*=7 Hz, CH(SPh)<sub>2</sub>),

6.2-6.5 (3H, m, ArH), 7.1-7.6 (10H, m, SPhH).  $^{13}\text{C}$ -NMR: 34.3, 34.9 (NCH<sub>3</sub>), 39.2, 39.4 (C1), 51.2, 54.1 (C2), 53.4, 53.7 (C3), 55.3 (OCH<sub>3</sub>x2), 99.4 (ArCH), 104.2 (ArCH), 105.8 (ArCH), 127.7 (PhCH), 127.8 (PhCH), 128.9 (PhCHx4), 132.5 (PhCHx2), 132.7 (PhChx2), 133.8 (PhC), 134.0 (PhC), 138.7, 139.4 (ArC), 161.0 (ArC), 164.4 (ArC), 169.4, 169.6 (C1). EI-LRMS  $m/z$ : 453 (M<sup>+</sup>, base peak).

Run 6: **6f** (200 mg, 0.58 mmol) yielded **7f** (99mg, 73%).

Run 7: **5g** (204 mg, 0.59 mmol) yielded **6g** (22 mg, 11%), **7g** (67 mg, 48%), **8g** (19 mg, 7%) and **10** (8 mg, 4%). Recovered **5g** (8 mg, 4%).

***N*-(2,3-Dimethoxyphenyl)methyl-*N*-methyl-*trans*-(3-phenylsulfonyl)acrylamide (6g)** A colorless gum. IR: 1635, 1558.  $^1\text{H}$ -NMR: 2.96 (3H, br s, NCH<sub>3</sub>), 3.79, 3.87 (total 3H, each s, OCH<sub>3</sub>), 4.50, 4.69 (total 2H, each br s, CH<sub>2</sub>NCH<sub>3</sub>), 6.27 (1H, br d,  $J=15$  Hz, olefinic H), 6.5-7.6(8H, m, Ar-H, and SPhH), 7.81 (1H, d,  $J=15$  Hz, olefinic H). EI-LRMS  $m/z$ : 343 (M<sup>+</sup>), 234 (base peak). FAB-HRMS (MH<sup>+</sup>)  $m/z$  Calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S: 344.1321, Found: 344.1315.

**8,9-Dimethoxy-2-methyl-1,2-dihydrobenz[*c*]azepin-3-one (7g)** Pale yellow prisms recrystallized from CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, mp 96-97 °C . IR: 1643, 1597.  $^1\text{H}$ -NMR: 3.11 (3H, s, NCH<sub>3</sub>), 3.90 (3H, s, OCH<sub>3</sub>), 3.91 (3H, s, OCH<sub>3</sub>), 4.40 (2H, s, 1-H), 6.27 (1H, d,  $J=12$  Hz, 4-H), 6.89 (1H, d,  $J=8$  Hz, 6-H), 7.00 (1H, d,  $J=12$  Hz, 5-H), 7.08 (1H, d,  $J=8$  Hz, 7-H).  $^{13}\text{C}$ -NMR: 35.1 (NCH<sub>3</sub>), 45.1 (C1), 55.8 (OCH<sub>3</sub>), 61.6 (OCH<sub>3</sub>), 111.4 (C4), 125.1 (C5), 125.6 (C7), 129.2 (C9a), 130.4 (C5a), 136.1 (C6), 145.1 (C9), 153.4 (C8), 166.8 (C2). UV: 279 (14600). EI-LRMS  $m/z$ : 233 (M<sup>+</sup>, base peak). FAB-HRMS (MH<sup>+</sup>)  $m/z$  Calcd for C<sub>13</sub>H<sub>16</sub>NO<sub>3</sub>: 234.1130, Found: 234.1135.

***N*-(3,5-Dimethoxyphenyl)methyl-*N*-methyl-3,3-diphenylsulphonylpropionamide (8g)** A yellow gum. IR: 1645, 1479.  $^1\text{H}$ -NMR: 2.7-3.0 (5H, m, NCH<sub>3</sub>, COCH<sub>2</sub>), 3.78, 3.81, 3.85, 3.87 (total 6H, each s, OCH<sub>3</sub>), 4.45, 4.69 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 5.14 (1H, t,  $J=7$  Hz, CH(SPh)<sub>2</sub>), 6.5-7.1 (3H, m, ArH), 7.1-7.6 (10H, m, SPhH). EI-LRMS  $m/z$ : 453 (M<sup>+</sup>), 151 (base peak).

Run 8: **6g** (204 mg, 0.59 mmol) yielded **5g** (6 mg, 3%), **7g** (77 mg, 55%), **8g** (13 mg, 5%) and **10** (3 mg,

4%). Recovered **6g** (22 mg, 11%).

Run 9: **5h** (200 mg, 0.58 mmol) yielded the mixture of **9** and **10** (1:9)(62 mg, 51%) and **7h** (1 mg, 1%)

**N-Methyl-cis-3-phenylsulfanylacrylamide (9)** Data of **9** were obtained from the <sup>1</sup>H-NMR spectra of the mixture (**9** and **10**). <sup>1</sup>H-NMR: 2.83, 2.85 (total 3H, each s, -NCH<sub>3</sub>), 5.76 (1H, d, *J*=10 Hz, olefinic H), 7.67 (1H, d, *J*=10 Hz, olefinic H), 7.4-7.5 (5H, m, SPh).

**7,8-Dimethoxy-2-methyl-1,2-dihydrobenz[c]azepin-3-one (7h)**<sup>6</sup> A pale yellow gum. IR: 3436, 1637. <sup>1</sup>H-NMR: 3.10 (3H, s, NCH<sub>3</sub>), 3.90 (s, OCH<sub>3</sub>), 3.95 (s, OCH<sub>3</sub>), 4.17 (2H, s, CH<sub>2</sub>NCH<sub>3</sub>), 6.33 (1H, d, *J*=12 Hz, olefinic H), 6.79, 6.85 (each 1H, s, Ar), 6.98 (1H, d, *J*=12 Hz, olefinic H). <sup>13</sup>C-NMR: 35.1 (NCH<sub>3</sub>), 53.1 (C1), 56.1 (OCH<sub>3</sub>x2), 110.4 (C6), 111.9 (C9), 126.0 (C4), 128.3 (C<sub>5a</sub>), 129.5 (C<sub>9a</sub>), 136.3 (C5), 148.8 (C7), 149.8 (C8), 166.6(C2). EI-LRMS *m/z*: 233 (M<sup>+</sup>), 233 (base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>13</sub>H<sub>15</sub>NO<sub>3</sub>: 233.1050, Found: 233.1037.

Run 10: **6h** yielded **9** (4 mg, 3%) and **10** (64 mg, 60%).

Run 11: **5i** (200 mg, 0.58 mmol) yielded **6i** (75 mg, 38%), **10** (30 mg, 26%) and **8i** (4 mg, 3%) and recovered **5i** (10 mg, 5%).

**N-(2,5-Dimethoxyphenyl)methyl-N-methyl-trans-3-phenylsulfanylacrylamide (6i)**. A Pale Yellow gum. IR: 1629 cm<sup>-1</sup>. <sup>1</sup>H-NMR: 2.92, 3.30 (total 3H, each s, NCH<sub>3</sub>), 3.74 (3H, s, OCH<sub>3</sub>), 3.75 (3H, s, OCH<sub>3</sub>), 4.23, 4.63 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 6.24 (1H, d, *J*=15 Hz, olefinic H), 6.6-6.9 (3H, m, Ar), 7.3-7.5 (5H, m, SPh), 7.77 (1H, d, *J*= 15 Hz, olefinic H). <sup>13</sup>C-NMR: 34.4, 35.2 (NCH<sub>3</sub>), 45.8, 48.8 (C1'), 55.6 (OCH<sub>3</sub>), 55.7, 55.9 (OCH<sub>3</sub>), 110.9, 111.3 (ArCH), 112.3, 113.9 (ArCH), 115.2, 115.4 (C2), 116.1 (ArCH), 125.9, 126.6 (PhC), 128.2, 128.5 (PhCH), 129.3, 129.4 (PhCHx2), 131.7, 132.0 (PhCHx2), 143.5, 144.2 (C3), 151.0 (ArC), 151.7 (ArC), 153.7 (ArC), 165.2, 165.8 (C1). EI-LRMS *m/z*: 343 (M<sup>+</sup>), 234 (base peak). FAB-HRMS (MH<sup>+</sup>) *m/z* Calcd for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub>S: 344.1321, Found: 344.1305.

**N-(2,5-Dimethoxyphenyl)methyl-N-methyl-3,3-disphenylsulfanylpropionamide (8i)** A Pale yellow gum. IR: 3401, 1641 cm<sup>-1</sup>. <sup>1</sup>H-NMR: 1.18 (3H, s, NCH<sub>3</sub>), 2.81 (1H, d, *J*=7 Hz, COCH<sub>2</sub>), 2.86 (1H, d, *J*=7

Hz, COCH<sub>2</sub>), 3.60, 3.66, 3.69 (total 6H, each s, OCH<sub>3</sub>), 4.32, 4.56 (total 2H, each s, CH<sub>2</sub>NCH<sub>3</sub>), 5.06 (1H, d, *J*=7 Hz, -CH(SPh)<sub>2</sub>), 6.6-6.8 (total 3H, m, Ar), 7.2-7.4 (10H, m, SPh). <sup>13</sup>C-NMR: 34.0, 35.3 (NCH<sub>3</sub>), 39.1, 39.2 (C1), 45.7, 48.9 (C2), 53.4, 53.9 (C3), 55.5 (OCH<sub>3</sub>), 55.7, 55.9 (OCH<sub>3</sub>), 111.0, 111.4 (ArCH), 112.8, 113.1 (ArCH), 113.8, 114.7 (ArCH), 125.1, 126.2 (ArC), 127.6, 127.8 (PhCH<sub>x2</sub>), 128.9 (PhCH<sub>x4</sub>), 132.4, 132.7 (PhCH<sub>x4</sub>), 133.8 (PhC), 134.1 (PhC), 151.1, 151.7 (ArC), 153.7, 153.8 (ArC), 169.6, 169.8 (C1). EI-LRMS *m/z*: 453(M<sup>+</sup>), 151(base peak). EI-HRMS (M<sup>+</sup>) *m/z* Calcd for C<sub>25</sub>H<sub>27</sub>NO<sub>3</sub>S<sub>2</sub>: 453.1433, Found: 453.1466.

Run 12: **5j** (314 mg, 0.95 mmol) yielded **10** (80 mg, 45%).

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